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(応力)

Stresses in Pt/Pb(,Ti)O_3/Pt thin-film stacks for integrated ferroelectric capacitors

ゾルゲルPZT

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BEの応力
アニール −750MPa→1GPa
PZTの応力 <200MPa

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A study of the stresses in a ferroelectric capacitor stack deposited on an oxidized silicon substrate is presented. The capacitor stack was prepared with sputtered Pt bottom and top electrodes and a ferroelectric film of composition $PbZr_xTi_{1-x}O_3$ (PZT) with $x \approx 0.5$ which was deposited using a modified sol-gel technique. The stresses were determined by the changes in the radius of curvature of the wafer following the deposition steps, during and after annealing treatments, and after etching steps in which the top electrode, the PZT film, and the bottom electrode were successively removed. The largest stress effects are found in the Pt electrodes which are deposited under conditions giving an intrinsic compressive stress. An annealing treatment exceeding 500 °C changed the stress of the bottom electrode from ≈ -750 MPa (compressive) to a large tensile stress (≈ 1 GPa). This stress is largely thermal and is caused by the differences in thermal-expansion coefficients of the Pt film and the Si substrate. The stress of the PZT film is numerically relatively small (below ≈ 200 Mpa) and it is found to be of both thermal and intrinsic origin. The deposition and annealing of the top electrode has a profound influence on the stress of the PZT film as well as on the electrical properties. The stress behavior of the as-deposited PZT film shows a poling direction mainly in the plane of the substrate. An annealing of the complete capacitor stack changes the poling direction of the ferroelectric film to be perpendicular to the substrate. This explains the observed electrical switching properties of as-prepared as well as annealed ferroelectric capacitors. © *1995 American Institute of Physics.*

TEアニール後の応力変化が大きく

圧縮応力でPrが低下しEcが増加する。

I. INTRODUCTION

The presence of stress in a ferroelectric thin film can be expected to influence the electrical properties of an integrated ferroelectric capacitor.[1] It is well established that stresses in Pb(Zr,Ti)O_3 ceramics influence properties such as dielectric permittivity, tan(δ), and piezoelectric coefficients.[2] The effects are most pronounced for compressive stresses applied parallel to the polar axis. PZT can react to an applied stress by 90° reorientation for the tetragonal and 109° and 71° reorientation for the rhombohedral phase.[1] This indicates the possibility of stress-induced effects in the switching behavior of a PZT film. Furthermore, excessive tensile stresses in the films may result in film cracking and edge delamination, and compressive stresses can result in buckling of the film.[3]

Stresses in ferroelectric thin films and their effects on some properties have been subjects of recent investigations. Desu showed that for $BaTiO_3$ films the hysteresis curve deteriorates (remanent polarization P_r decreases while the coercive field E_c increases) when the film is compressively stressed.[4] Tuttle *et al.* found similar effects for PZT films. The compressive PZT films deposited on sapphire exhibit superior ferroelectric properties as compared to tensile films deposited on silicon substrates.[5] Tuttle *et al.* suggested that the stress conditions at the Curie point determine the crystallite/domain orientation within the PZT film and consequently the ferroelectric behavior.

キュリー点で一結晶配向が強誘電特性を支配る

圧縮の方が良好な強誘電性を示す

In this paper the evolution of stress during processing of a ferroelectric capacitor prepared with Pt bottom and top electrodes and sol-gel $PbZr_xTi_{1-x}O_3$ ($x \approx 0.5$) film on an oxidized Si substrate is reported. The materials and processing conditions used in this investigation are the result of an extensive study directed toward optimizing the properties of the ferroelectric capacitor for nonvolatile memory applications.[6–8]

First, the stress after deposition and after annealing treatments is determined for each film. Second, the influence of interactions between the different layers of the capacitor is described on the basis of stress data obtained from a step-by-step removal of the films in the completed capacitor stack. Finally, the effects of stresses in the PZT film prior to and after the top electrode annealing on the switching behavior of the capacitor are discussed.

II. EXPERIMENTAL METHODS

A. Thin-film deposition and etching

The bottom electrodes, which consisted of a 4 nm adhesion-promoting Ti layer and a 70 nm Pt film, were sputter-deposited on 100 mm diameter oxidized silicon wafers using a Nordiko NS2050 sputter system without substrate heating. However, during deposition some heating of the wafer to about 60 °C is unavoidable. The properties of these electrodes in relation to the PZT deposited on top of them have been described in more detail in Ref. 6.

PZT films with compositions near the morphotropic phase boundary ($x \approx 0.5$) were deposited by a modified sol-gel technique.[7] The process consisted of three spin-coated

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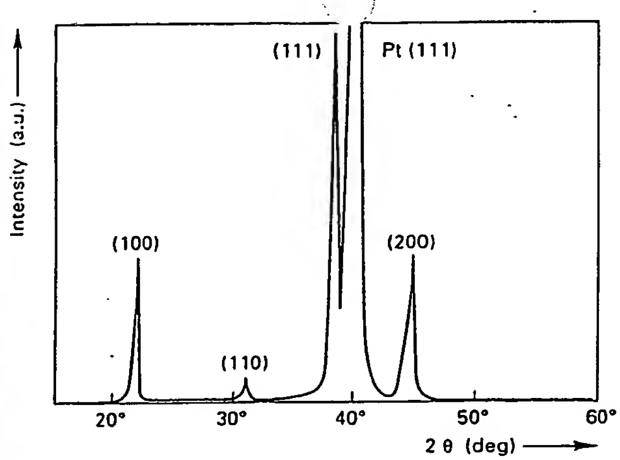

FIG. 1. X-ray-diffraction pattern of PZT used in this investigation.

layers with thicknesses of 90, 65, and 65 nm, respectively. After deposition of each layer a bakeout treatment was applied. This consisted of a 30 min heat treatment in N_2/O_2 at 550 °C for the first layer and at 600 °C for the other two layers. The deposition was completed with a final annealing (650 °C, N_2/O_2, 30 min). The x-ray-diffraction pattern (Fig. 1) shows that in the PZT film all crystallite orientations are present but that there is a preferential orientation in the (111) and to a lesser degree in the (100) direction. The composition is too close to the morphotropic phase boundary to show any splitting of the (100) or (200) peaks. It was pointed out in Ref. 7 that the splitting of (h00) and (00h) lines in the diffraction pattern of tetragonal PZT close to the morphotropic phase boundary (where the splitting becomes small) is obstructed in fine grained films due to the broadening of the diffraction lines.

The top electrode (70 nm Pt+7 nm Ti) was sputter-deposited with the same conditions as used for the bottom electrode. The Pt film was etched by ion-beam milling[9] and the PZT film was wet chemically etched.

B. Stress measurements

Stress in a thin film deposited on a circular substrate results in a spherical warpage of the substrate. A commercial stress analyzer (Tencor FLX-2900) was used to measure this warpage with a laser-reflection system. This analyzer can measure the warpage of the wafer *in situ* during heating to 900 °C. The total stress σ in the film can be calculated from the difference in the radii of curvature before (R_0) and after (R) a particular processing step (e.g., deposition or annealing), using the Stoney formula[10]

$$\sigma=\frac{E_s}{6(1-\nu_s)}\frac{t_s^2}{t_f}\left(\frac{1}{R}-\frac{1}{R_0}\right), \tag{1}$$

where t_f is the film thickness and E_s, ν_s, and t_s are the elastic modulus, Poisson ratio, and thickness of the substrate, respectively. Negative values for σ indicate a compressive stress and positive ones a tensile stress. Two types of measurements were used in this investigation. First of all, the stress was measured at room temperature after a specific processing treatment as a function of the processing parameters. Second, *in situ* stress measurements were carried out with the stress analyzer while the film underwent a thermal cycling process. The latter had to be done in N_2, since stress measurements in oxygen-containing atmospheres were not possible at temperatures above a few hundred degrees Celsius.

TABLE I. Young's moduli (E_s) and Poisson ratio (ν) of Pt (see Ref. 11), unpoled polycrystalline PZT (see Ref. 13), and Si (see Ref. 12).

	E_s (GPa)	ν_s
Pt	170	0.39
PZT	72	0.30
Si	130	0.28

The application of Eq. (1) for calculating the stress in a particular film requires that the substrate and any previously deposited films not be influenced during the deposition of the film under study. Possible effects in the substrate and underlying films include recrystallization, interdiffusion, chemical reaction, and plastic deformation processes. Such processes are likely to occur during an anneal treatment in any of the films in a stack. In order to isolate the effects in one particular film without interference from changes in the stress-related conditions within any of the other films, the stress is measured before and after removal of the film, e.g., by etching. In this way the effects of an anneal treatment in a particular film can be determined separately from changes in other films. The total stress in a multiple stack is the sum of the stresses in each film.

In general several different stresses contribute to the total stress;[3] the intrinsic stress σ_{int} and the thermal stress σ_{th} are the most relevant ones for this investigation. The intrinsic (or growth) stress is the result of the accumulation of structural imperfections that are built into the film during the deposition process. Its magnitude is largely determined by the thin-film deposition conditions. Generally, when films are annealed the intrinsic stresses are reduced by interdiffusion, recrystallization, and grain growth processes. On subsequent cooling (to room temperature) a thermal stress is introduced. The thermal stress originates from the difference in thermal expansion between the substrate and the thin-film material over the cooling range from an annealing temperature T_{anneal} to a temperature T_0. It is given by

$$\sigma_{\mathrm{th}}=\frac{E_f}{1-\nu_f}\int_{T_{\mathrm{anneal}}}^{T_0}(\alpha_f-\alpha_s)dT. \tag{2}$$

E_f and ν_f are the Young's modulus and the Poisson ratio of the film material. These properties are given in Table I. α_f and α_s are the thermal-expansion coefficients of the film and substrate, respectively. For this study the thermal-expansion coefficient of Pt and Si given in Refs. 11 and 12, respectively, are used. For PZT we used the data reported by Cook, Jr., Berlincourt, and Scholz for bulk material with composition $PbZr_{0.52}Ti_{0.48}O_3$ doped with 1% Nb_2O_5.[13] Figure 2 shows the thermal-expansion coefficients for unpoled PZT (α), for poled PZT perpendicular (α_1) to the poling direction,